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Photophysical properties of thin films and solid phase of switchable supermolecular anthracene-based rotaxanes

G. Giro[a], M. Cocchi[a], V. Fattori[a], G. Gadret[b], G. Ruani[b], M. Cavallini[b], F. Biscarini[b], R. Zamboni[b,*], T. Loontjens[c], J. Thies[c], D.A. Leigh[d], A.F. Morales[d], R.F. Mahrt[e]

[a]*FRAE-CNR, via P. Gobetti 101, 40129 Bologna, Italy*
[b]*ISM-CNR, via P. Gobetti 101, 40129 Bologna, Italy*
[c]*DSM Research, P.O. Box 18, 6160 MD, Geleen, The Netherlands*
[d]*CSMC, Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK*
[e]*MPI fur Polymer, Ackermannweg 10, 55021 Mainz, Germany*

Abstract

Polycrystalline powders and thin films of a novel rotaxane, methyl-exopyridine-anthracene rotaxane (EPAR-Me), and of the related thread and stoppers 10-[3,5-di (ter butyl)phenoxy]decyl-2-({2-[(9-anthrylcarbonyl) amino] acetyl}amino) acetate (ANTPEP), have been characterised by photoluminescence, absorption and photoluminescence excitation spectroscopy. A rather unusual, i.e. unstructured and largely red-shifted, photoluminescence spectral behaviour of the rotaxane has been found. Preliminary time resolved measurements indicate a fast energy transfer from the anthracene unit to different species the nature of which is still not assigned.

Keywords: Rotaxanes; Thin film; Solid state spectroscopy

1. Introduction

Rotaxanes are a novel class of mechanically interlocked molecules (supermolecules) where intrinsic functions can be designed for specific uses. Schematically, they consist of a macrocycle constrained on a thread by two stoppers. The macrocycle could in principle move from one end to the other of the thread, rotate around it or stay at one particular point on the thread. Hydrogen bonding also plays a major role both in synthesis and in determining the location of the macrocycle in the supermolecule [1]. The chemical synthesis is extremely flexible allowing individual blocks with particular function to be designed in a kind of ''molecular meccano'' fashion [2]. Movement or activation of the interlocked components could give rise to well controlled electron transfer or energy transfer. There is a rather large and growing literature on supermolecular systems in solution but a small amount of work has been reported addressing the solid state properties [3]. In this work, we have studied the photophysics of a novel rotaxane, namely the methyl-exopyridine-anthracene (EPAR-Me) rotaxane, in the solid state.

The chemical structure of the investigated compound is shown in Fig. 1. The system consists of a macrocycle including two symmetric methylpyridinium groups, threaded by a peptide group covalently bonded to a linear (CH_2) chain. The two stoppers constraining the macrocycle are an anthracene moiety at one end of the thread and a bis-terbutyl benzene ring as the other.

The thread and stoppers unit, i.e. 10-[3,5-di (ter butyl)-phenoxy]decyl-2-({2-[(9-anthrylcarbonyl) amino] acetyl}amino) acetate (ANTPEP), is shown in bold in Fig. 1.

2. Experimental results and discussion

Absorption and photoluminescence excitation (PLE) spectra of spin-coated thin films and polycrystalline powder of EPAR-Me rotaxane and of ANTPEP are reported in Fig. 2.

For both EPAR-Me and ANTPEP, the absorption spectra show a well-resolved progression of electronic transitions. We note a fairly good correspondence with the absorption spectrum of anthracene crystals. Comparing the PLE spectra of both, we note a different behaviour.

The PLE ANTPEP spectrum shows a perfect coincidence with the absorption spectrum whereas for the EPAR-Me a new broad low-lying band appears in the PLE. This new

* Corresponding author. Tel.: +39-51-639-8514; fax: +39-51-639-8540.
E-mail address: zamboni@astbo1.bo.cnr.it (R. Zamboni).

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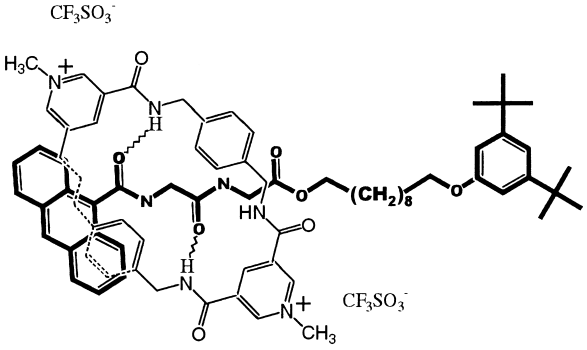

Fig. 1. Chemical structure of the methyl-exopyridine-anthracene rotaxane (EPAR-Me). The 10-[3,5di (ter butyl)phenoxy]decyl-2-({2-[(9-anthrylcarbonyl) amino] acetyl} amino) acetate (ANTPEP) unit is shown in bold.

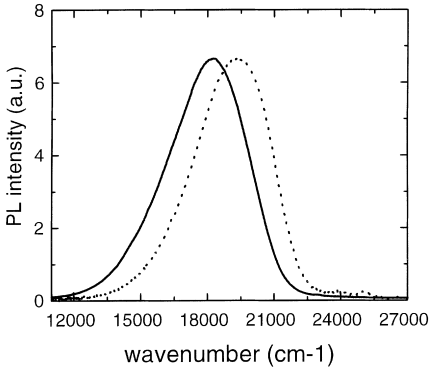

Fig. 3. PL spectra of polycrystalline powders of EPAR-Me at 293 K (solid line) and 4.2 K (dotted line). The excitation energy is 27,360 cm^{-1}.

band, indicated by an arrow in Fig. 2, remains at the same energy when the temperature of the sample is lowered to 16 K. It is worth noting that at low temperatures this new feature, shows an increased intensity contribution to the overall integrated spectrum. Both PLE spectra are independent of the detection wavelength. The EPAR-Me PLE behaviour is reversible with temperature.

The observation of the new feature in the EPAR-Me PLE spectrum indicates the presence of emitting species in the ground states [4] which are not measurable in the absorption spectrum due to their low concentration.

In Fig. 3, the steady-state PL of EPAR-Me is reported. The spectrum consists of a structureless broad band peaked at around 18000 cm^{-1}. The characteristic vibronic progression

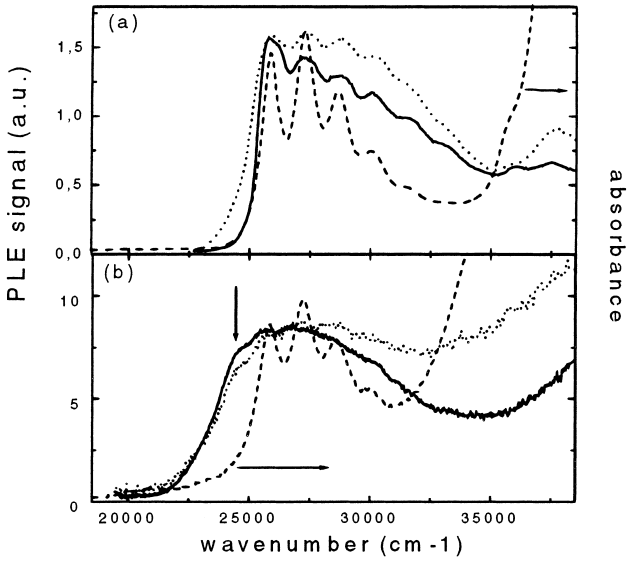

Fig. 2. (a) PLE of ANTPEP polycrystalline powder at 293 K (dotted line) and 16 K (solid line) compared to the room temperature absorption spectrum of a film spin coated from a solution of dichloromethane (dashed line); (b) PLE of EPAR-Me polycrystalline powder at 293 K (dotted line) and 16 K (solid line) compared to the room temperature absorption spectrum of a film spin coated from a solution of ethylacetate (dashed line).

of the anthracene moiety is totally lost and the spectrum is largely red-shifted. When the sample temperature is lowered at 4.2 K the maximum of the PL is blue-shifted to 19500 cm^{-1}.

This behaviour suggests that for the EPAR-Me the emission may occur from different species involving the supermolecular nature of the investigated system in the solid state. It is noteworthy that the EPAR-Me in solution shows the anthracene-like behaviour. Preliminary results of time-resolved femtosecond PL spectroscopy on polycrystalline EPAR-Me show a fast energy transfer (few tenths of picoseconds) from the anthracene units to other long living species.

The decay process is bi-exponential supporting the existence of different species with different decay times.

In conclusion, we have performed a spectroscopic characterisation of a novel rotaxane, the EPAR-Me with the aim of assessing the photophysics in the solid state.

The supermolecule possesses units that can give rise to controlled electron transfer and/or energy transfer. We have found a considerable deviation of the PL behaviour from the fluorescence emission characteristics of the main chromophore unit (anthracene) present in the supermolecule. The unstructured largely red-shifted PL spectrum may indicate that electron transfer and/or excimer-like or exciplex-like species are possibly responsible for the radiative decay process.

The clear presence of low-lying emitting species in the ground state could be due to molecular aggregates (charge transfer, neutral intra-supermolecular or inter-supermolecular defects, etc.) the nature of which is not yet understood. Further experiments are in progress in order to get a better comprehension of the supermoleucar system in the solid state and processes occurring therein.

Acknowledgements

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